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INTEGRATED REAL TIME CONTAMINATION MONITOR

IRTCM

Center for Environmental and Energy Studies



The University
Of Alabama
In Huntsville

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INTEGRATED REAL TIME CONTAMINATION MONITOR
IRTCM

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May 1976

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SUMMARY

Engineering and design work was performed on a monitoring device for particulate and gas contamination to be used in the space shuttle cargo area during launch at altitudes up to 50 km and during return phases of the flight. The gas sampling device consists of ampules filled with specific absorber materials which are opened and/or sealed at pre-programmed intervals. The design eliminates the use of valves which, according to our experiments, are never sealing properly at hard vacuum (limit 10^{-5} torr).

Methods of analysis including in-flight measuring possibilities are discussed.

INTRODUCTION

The following report is the result of an engineering and design approach taken by the Center for Environmental and Energy Studies of The University of Alabama in Huntsville for NASA/Marshall with the purpose to develop a contamination monitor package to be used in the cargo bay area of the Space Shuttle. The package consists of a multitude of sampling devices, more or less specific, to absorb certain gases for post analysis (after flight completion). Real time analysis is possible by using an in-flight mass spectrometer similar to those designs used in previous moon flights or Mariner Mars missions.

As NASA had already decided to use a quartz/oscillator bridge system for particulate analysis by mass determination, the only concern for our work was gas sampling. Two different devices were developed: one, a grab sampler using an absorber-filled small tube inside a larger glass cylinder which contained a second absorber and cryo-pumping material in its lower half. The second device serves as a "continuous" sampler and consists of one or several tubes filled with absorbing material and is connected to a vacuum manifold. At a given time span, connection to the cargo area atmosphere is made after which the sample obtained is hermetically sealed for post-flight analysis.

The grab sampler was developed first for the purpose of ozone analysis of the upper atmosphere. It was planned to use such a grab sampler array for a balloon flight and analyze the ozone level by introducing a small but adequate sample of high purity ethylene gas into the sampler at the same time the atmospheric sample was taken. For this purpose, a number of valves were bought, tested, re-designed and re-tested, and found totally inadequate for vacuum levels below 10^{-5} torr. This bad experience resulted in a complete elimination of valves for grab and "continuous" samplers. The basic concept consists of replacing the valves with an ampule system consisting of a magnetic ampule smasher to open, and a thermo-electric sealing system to close the sampler.

For the ozone sampler, it is not feasible to use the ampulating approach because of the fire hazard involved with the ethylene or its oxide. A valve has to be used here. The following approach is suggested:

1. Sampling should occur during the return flight of the shuttle. Here, outside pressure increase is seen rather than decrease so that no leak can occur to the outside.
2. Valves and ethylene bottle should be enveloped entirely into a glass sealed (fused) envelope with a magnetic ampule smasher opening this system to the outer atmosphere. This assembly would fly "sealed" the entire way, evacuated to a 10^{-7} torr level and be opened upon descent at proper altitude.
3. After sampling has occurred, no thermal sealing of the grab sampler is required. A mere closure of the valve prevents dilution or evaporation of the sample.

Glass (Pyrex) is to be used predominantly for the design of the sampler in itself, and any exposure of the sample to any kind of metal is avoided as much as possible. The reason for this is obvious, as practically all metallic surfaces show a very high wall absorption effect. With glass and Teflon, this wall effect is minimized according to EPA and a number of researchers.

Originally, we proposed to design and test a membrane pump to generate the vacuum required for the continuous sampler. This approach was postponed because of the urgency of the grab sampling design for the balloon flight test. It was decided to use a commercial design that was said to operate up to pressures of 0.5 micron pressure. For higher altitude, the cryo-pumping effect of the molecular sieve 5-A of the sampler packing would then be able to take over until the vacuum would be so hard that no more sampling would be possible.

The use of specific color reactions by impregnating a silicagel or similar material with appropriate reagents remains still feasible, providing that:

1. The reaction is stable with time or can be measured soon after formation; and
2. If stable, the sampling tube will have to be amputated to prevent evaporation into the hard vacuum in the space shuttle cargo area at higher altitude. Thus, the reagent's vapor pressure limits the use of such a sampler also at higher altitude. Upon re-entry, this approach again is feasible.

3. For in-flight analysis, the system requires a colorimeter with monochromatization (light-filters) for each color test required and a simple recording mechanism or data transmission to ground.

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PURPOSE

The purpose of this developing approach was to provide a system capable to analyze for particulates and contaminating gases which could be found in the Space Shuttle Cargo Bay Area before and during launch, in-flight, upon return to Earth orbit, and during transit from the point of landing to the Cape for re-furbishing. This system had to be designed as a package to fulfill the requirements for a fast exchange for two reasons: one, to permit fast delivery of gas sample vials, particulate samples and recorded material for post-flight analysis to the laboratory; and secondly, for the matter of fastest re-furbishing to obtain continuous information of the contamination level without prolonged interruption between tasks. Thus, the monitor should consist of a quick connect/disconnect interchangeable module that allows interchangeability with the shortest possible time without sacrificing the precision of samples taken or subsequent sampling to be performed.

Measuring Parameters and Requirements

Contamination information is required to maintain integrity of cargo to be placed into orbit and to be delivered to the Space Station or orbital laboratory and to return products of such outer space stations back to Earth without changing the mechanical, chemical, metallurgical or biological property of the cargo. A typical example of such a contamination is seen in the formation of natural oxide films on metal surfaces which, like in aluminum for instance, leave an extreme absorption property of either hydrophillic or oleophillic nature depending on the history of formation. Thus, the oxide film can become acceptor for either one of the gaseous contaminants, forming a barrier layer which determines the degree of corrosion protection to Earth's atmosphere. It is apparent, in this case, that if oleophillic material has been absorbed by the aluminum oxide-hydrate layer a better corrosion protection against subsequent exposure to salt spray and inorganic acidic exposure will be observed. On the other hand, such oleophillic surface contamination will evaporate in the space environment and, thus released from its surface, be available in the environment of the cargo area where higher absorbing material and/or temperature difference could generate another contamination problem.

The following parameters are to be measured within a flight schedule from pre-launch through return for re-furbishing to the Cape:

Temperature	Liquid and Gases from
Humidity	Hypergolic System
Barometric Pressure	Liquid and Gases from
at Cargo Bay	Hydraulic System
Particulates	Particulates and Gases
Dew Point	from Rocket Exhaust
Condensable Moisture	De-gasing products from
Total Hydrocarbons	Cargo
Ammonia	Silicones from lubricants, etc.
	Halogenated Hydrocarbons (residual cleaners)
	Air Gases: N_2 , CO_2 , O_3 , He
	De-gasing products from ablative material, Cargo Bay insolation and stored cargo

The requirements to measure the parameters listed above are depending on several practical conditions. In order to observe such contaminants, it has to be considered:

- Where they are most likely to appear during flight
- At what partial pressure in the cargo area they have to be measured and at what temperature
- What are the chances of their reaction with other contaminants present at the same time
- What sampling rate (flow rate, density, temperature and humidity), controlling orifice and pumping efficiency can be achieved at that time and, finally
- How stable is the collected product if part-flight analysis is required.

Most of these criteria are flight dependent (i.e., depending on increase or decrease of pressure and temperature), but these factors determine also the availability of gaseous molecules per unit volume and their collision with each other to form new products.

The cargo area will be lined with an 8-layer fabric lamination buildup of 8.85 mils total thickness consisting of Teflon, Aluminum, Kapton Polyimide Film, and PRD 49 (plain weave cloth) which are sandwiched with each other using polyester adhesive. This insulating material will delay the heat transfer from the outside walls of the vehicle to the bay in flight. As the cargo bay is not built to accept large internal pressure, equalization of pressure difference is provided by filter protected openings; the largest filter panel measures 60" x 90" with a 2 inch thick insulation built into a fiber glass frame. Bulkheads are provided over these panels, and the bulkheads can be opened or closed during certain phases of the flight such as staging of the solid propellant motors after launch. This is to occur at an altitude of approximately 43 km (140,000 ft.) at a pressure of 0.028 PSI. As not all cargo bay openings to the outside are closed by bulkheads ("passive" vents also exist), the possibility exists that contamination may occur through these vents as exhaust products of these motors envelope the vehicle upon staging. As the two (2) main environmental factors, temperature and partial pressure, inside the cargo bay area are not precisely known at certain phases within the flight, they have to be measured and recorded in real time relation to the actual sampling performed. These two factors would permit flow calculations for gaseous samplers which, in turn, can be calculated effectively into quantitative product analysis. Before these data are available, only a qualitative or semi-quantitative analysis of the contamination products is feasible.

Nature and Origin of Anticipated Contaminants

The contaminants present in the pre-flight, launch, ascent, descent, landing, and Earth-transit phase will involve the three (3) states of matter: solid, liquid and gaseous. While solids are expected to be stable to a certain degree during the flight phases (except for out-gasing or dehydration), this is not the case for the liquid or gaseous material. Evaporation, distilling and dissipation will occur when samples are taken at Earth atmosphere level and submitted to outer space vacuum condition. It is, therefore, essential to hermetically seal sampling devices that operated at a known "ambient" pressure condition on the way to outer space. This statement does not hold true for the reverse condition (return flight), where the ambient pressure inside the cargo area does increase. We found that valves can seal with a minimum leak at pressures of 10^{-5} torr, and thus are applicable for sampling within this and higher pressure conditions.

The following is a list of contaminants which can be expected during flight or on ground level operations:

A. SOLIDS

Sand, salt, glass fibers, organic fibers (filters, insulation), metal flakes, pollen, human debris (hair, operator) before lift-off. Then, solid rocket fuel residues (inorganic salts, oxidizer aluminum flakes, un-burned fuel, carbon from plastic binder, ceramic debris like MgO , Al_2O_3 , in particular during staging. Delamination debris from wall insulation and cargo.

Delamination material generated in high vacuum region or generated by vapor-pressure release of surface-coated material (paint). Free-floating particulates under near zero or zero gravity conditions.

Upon return: With increased outer pressure, a back-flushing of the air filter might occur showing a repeat of part or all of the above mentioned matter upon re-entry into the Earth's atmosphere unless these filters have been changed and disposed of.

It is assumed that the bulkheads are now closed over the larger filter panels to eliminate contamination caused by retro-rocket firing. In order to achieve breaking of the velocity of re-entry, the shuttle will have to fly backwards, i.e. the engine cluster up front. The rocket engine plume and any ablative material of the outer skirt of the vehicle will result in the emission of gaseous and solid particulate matter of high concentration and of a variety within size distribution of solids of metal oxides by nature. As no information about the retention of the filter material was available at the time of this writing, no prediction about the transfer of such material through the filters without bulkhead protection can be made.

B. LIQUIDS

The liquid state will consist predominantly of water, either condensed humidity from the air or dumped from fuel cells or manned cabins. A certain amount is also generated during rocket burn. Leaks of the hydraulic fluid systems are the next largest source. Most of this matter will evaporize as altitude is gained. Upon return, and as low temperatures prevail in comparison to the outer atmosphere, condensation of water vapors can be anticipated as ambient atmosphere flows back into the cargo bay.

C. GASES

Gaseous products within the cargo area will be in abundance. "Atmospheric" gases are prevailing at launch, depending upon the quality of the purge gas used after cleaning and during loading of the cargo area.

Upon ascent, out-gasing of cargo and cargo-area materials will be observed, generating an increase in hydrocarbons (wall insulation and binder, cleaning solvents remnant on surfaces with natural oxide films, etc.). These gases will increase at staging, for a short time, but a rapid dissipation is anticipated from thereon as the ventilating hatches will be open after staging has occurred. At this altitude, sampling of gases by absorption becomes impractical because of the decrease of gas pressure. At this point, mass-spectrometric methods become feasible for in-flight measurements using "open" instrument design with an ion-getter pump. From here on out, it can be safely assumed that, with increasing vacuum to a maximum of 10^{-13} torr, a de-contamination of the cargo bay area and its payload will occur rather than a contamination.

The opposite is valid upon re-entry. Grab and continuous samplers become effective again from levels below 50 km altitude, and the open mass spectrometer begins to fail to operate because of inadequate vacuum. The chances of re-contamination increase with pressure and availability of gases generated by burning (complete or incomplete) of the various rocket motors using monomethylhydrazine, nitrogen tetroxide and jet fuel. In addition, there will be gaseous products generated from ablative material applied to the outer hull of the surface. Together with these products, the atmospheric gases available at this altitude (Ozone) will find access into the cargo bay through any filter not protected by a hatch. Pressure equalization will occur relatively fast with descent from this point on, and the temperature rise inside the cargo area will also be rapid. This condition can thus be considered the most contaminating situation during the entire flight period. As with gas and particulate contaminants and high cargo area atmospheric temperature but cold cargo, the condensation of liquids, the reformation of natural oxide films on metals and subsequent increasing capability to absorb gaseous matter is an extreme favorable condition for re-contamination.

Absorber Systems

In-flight analysis of air samples requires mass spectrometers or gas chromatograph-mass spectrometer combinations with an input for known volume of gas increasing with altitude, a vacuum pump system and electronics for data acquisition and retrieval. This approach, being voluminous, generates a space and weight problem, in particular when backup instrumentation is required. Thus, the idea of reducing the instrumentation to a number of small grab or continuous samplers was pursued, operating in the lower region of the flight where pressure conditions make sampling still feasible.

Grab samplers have been used successfully without cryogenic pumping to an altitude of 35 km by workers of the National Center for Atmospheric Research in various balloon flights.¹ By then, as the collected sample becomes smaller with altitude, considerable interference of out-gasing of the cylinder walls was observed which was overcome only by careful de-gasing and collection of a large sample volume using cryo-pumping with liquid helium.² The authors used 16 stainless steel cylinders, each 70 cm long and 3.8 cm diameter, which were partially immersed into liquid nitrogen contained in Dewars.

Outer space sampling has been performed previously on Skylab 4, but only for the spacecraft's atmosphere.³ Here, concentration methods were used by pumping the atmosphere of the lab through absorbing material (TENAX GC) using the pressure difference between the lab area and the hard outer space vacuum as a pump while controlling the gas flow by means of "sonic" flow through a small orifice. The choice of absorbing material went in favor of TENAX because of the relative insensitivity of this material to water which would otherwise interfere with the absorption of organic volatiles. As water is in abundance in man-occupied areas, it would pre-occupy the absorbing material and the absorber would be overloaded within a short time leaving no space to sample the hydrophobic organic material.

The use of organic high-polymer material as an absorber for gases or organic vapors is not new. This type of material has been in use in gas chromatographs for the past 6 years. High-polymer, stabilized compounds such as modified polystyrenes, Teflon, Diphenylphenylene oxide (known under the trade name of Porapak), and Tenax (TENAX GC = porous polymer of 2, 6 diphenyl-p-phenylene oxide) are used as packing material of gas⁴ chromatographic columns because of their hydrophobic absorption and the possibility of manufacturing them in almost perfect spherical shape to any required mesh size. For the gas

chromatographer, this eases the packing density per column length and thus the pre-determination and reproduction of the platen count or retention time of a gas-chroma column.

While hydrocarbons and organic vapors are absorbed on such polymers, retention and absorption of hydrophyllic vapors (water, ammonia, nitric acid, etc.) is obtained on inorganic material. One of the best known material of this kind is the Zeolites, highly porous "ceramics" of the composition SiO_2 , Al_2O_3 , Na_2 . These are excellent water and gas absorbers and are known under the trade name "molecular sieves." Their surface area is in the order of 600 - 900 square meters per gram, and they are known as excellent cryo-pumping material and widely used for this purpose. Water absorption property is in the order of 20 - 30% by weight absorber.

Thus, the property of both materials combined was the choice for the design for a grab sampler and the packing of a "continuous" (flow-through) sampler which could be used for an altitude up to 50 km with cryo-pumping.

IN-FLIGHT ANALYSIS

Colorimetry

The use of color changing reactions for in-flight analysis is very limited because of stability and volatility of its reagents, when used at high altitude or in outer space. It becomes feasible, however, upon re-entry because of pressure increase in the cargo bay area and because of the relatively short time before landing where samples could be removed for colorimetry if not performed on board. While quantitatively not very precise, this system would be ideal for an indication of presence or absence of certain gases or vapors at this time and could eliminate expensive and tedious gas chromatographic separation. Relative stable test reactions have been developed by such companies as Mine Safety Appliance, Draeger, and others. If a colorimeter is required aboard, a system could be developed whereby a number of tubes are mounted onto a rotating table which would permit stepping from sample tube to sample tube to perform in the following sequence:

1. Opening of sampling vial at both ends
2. Apply suction of air through vial
3. Monochromatize and standardize light beam
4. Readout of absorption and recording

Step 2 and 3 could be performed simultaneously. The number of samples would determine the size of the instrumentation. The reagent(s) required would be absorbed on a clear quality silicagel of known light transmittance used in the standardization.

Mass Spectroscopy

Mass Spectroscopy is still the best in-flight and post-flight analysis method available today. As NASA has used "open" instrumentation on a number of flights before, it is not necessary to repeat the operation and sensitivity of these instruments. For higher atmospheric pressure, "open" designs are not feasible, of course, and the system becomes bulky and

heavy. Besides the Ion pumps, a Forevac pump (roughing pump) has to be used or cryogenic pumping applied. Therefore, the decision was made to use grab samplers or continuous samplers wherever possible. These then would be analyzed in a laboratory upon return.

Instrumentation

Gas and/or vapor samplers consist of inert tubing filled with absorptive material. At both ends of the tube, valves or other shutoff devices have to be located to permit flow of the gases through the collecting device. Capability to heat the sample tubing is required for bakeout, de-gasing of its contents or, after use, to free accumulated gases for analysis. This has to be considered in materials design of the sampler. For high altitude or space use, the leakage has to be considered also. The safest (and inexpensive) way here is to avoid valves entirely and use ampulation which permits hermetic seals better than any valve.

Two types of samplers are proposed for use in the Space Shuttle Cargo Area: a grab sampler (for short intervals of sample timing) and a continuous sampler. For the planned ozone analysis and balloon flight test, a valved grab sampler was designed for two reasons: one, the ampulation system could generate a fire hazard as Ethylene gas is introduced purposely into the sampling system; and second, there could be an oxidation of the ethylene generated which would cause a misreading or misinterpretation of analytical results.

The ampulation method has to permit both opening and closing of the sampling device. Opening is achieved by breaking away (mechanically) the tip of the ampule. Closing is obtained by a short high current melting loop around the thin neck of the glass ampule. Mechanical or electromechanical devices can assist both operations. Development of this system was not performed as yet, as the failure of the valves generated this line of thought late in the contract when both time and money were running out. The illustration on the following page shows how this method could be applied.

The choice of glass as working material is the result of experiences gained by EPA and others. Except for water vapor, the wall absorption for gases either inorganic or organic by nature is at a minimum. Hydrofluoric acid with water vapors present generates a reaction on the glass wall; and for this type combination, stainless steel is better, of course. Stainless steel, however, and any passive layer willfully generated on its surface, has a high absorption for hydrocarbons and some inorganic gases which makes even bake out a problem.

The following steps describe the operation of the ampulation sampler:

1. With the vacuum pump on and operating into a manifold to which the sampler is connected at its bottom outlet (this one still closed), the upper opening device becomes energized and opens the sampler. Air is taken into the sampler through the flow restrictor F, until pressure equalization occurs.
2. The lower opening device is energized and connects the sampler with the pump through the manifold; sampling continues.
3. After elapse of required sampling time, the heater filaments are energized (pump side first) and a spring tension device (not shown on illustration) bends both the intake and pump end of the small tubing of the sampler to assure hermetic sealing of the ampule.
4. The sampler can now be removed for post-flight analysis at any time desired.

Post-flight analysis requires re-opening of fused ends, purging the contents with helium or other carrier gas into the GC-MS system following by bake out under carrier gas flow to a temperature of 250° Centigrade.

IECM INSTRUMENTATION REQUIREMENT DEFINITION

Description of Instrument

The instrument consists of an interchangeable package, holding sensors for particulate matter, dew point determination, moisture and temperature determination, and gas samplers. Two types of samplers are used: grab samplers for short time/large volume sampling, and continuous samplers which run over a longer period of time during launch, ascent and descent up to vacuum conditions of 0.5 m/m Mercury.

Grab Samplers

The design uses a pre-degased and evacuated pyrex bottle divided into 2 compartments by a glass frit and glass-threaded openings on both ends. These ends carry valves or ampulating facilities to open access to the environmental atmosphere and to hermetically close the sampler after performance. The absorption material consists of gas-chromatic packing of a small glass tube at the inlet (upper part of sampler) and an inorganic absorption and cryogenic pumping material confined in the lower part (under the frit) of the bottle. The packing material may be selected to a specific purpose, such as hydrocarbon compounds, oleophillic material to be absorbed on one of the Porapaks or Tenax GC, and hydrophillic material and water on molecular sieves (A-5). Figure 1 shows a grab sampler designed for ozone measurements.

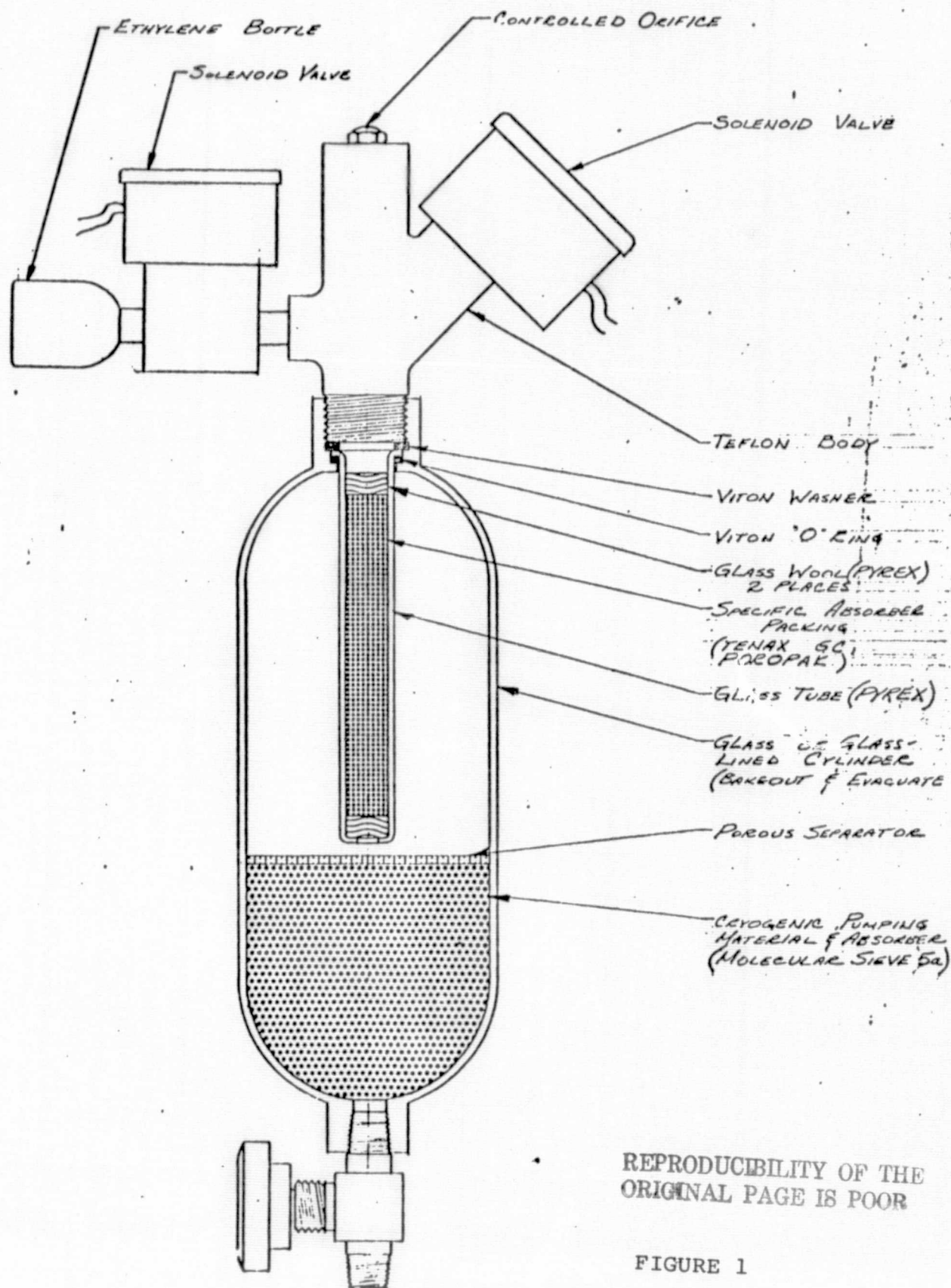
Continuous Samplers

The continuous sampler consists of a double tube system packed in a similar manner as in A, i.e., with oleophillic and hydrophillic absorption material. The tubes are connected at the bottom to a manifold which, in turn, is connected to a membrane pump capable to perform in the low pressure region described. Both ends of this sampler are protected after out-gasing until use by ampule-type seals, and a second set of seals is provided for closing the sampling tube after the sampling performance. For closing, the inlet orifice is heated by a filament from the outside of the tube until the restriction provided does collapse under the vacuum supplied by the pump. Then, the lower (pump side) restriction is closed in the same manner. See attached sketch of the ampulation system (Figure 2).

Performance Analysis

There will be 3 main phases of collecting: launch, ascent and descent. Of these, or any in-between scheduled sampling periods, the most critical will be the ascent period, as a relative rapid pressure drop occurs, and the amount of sampling material and contaminating material becomes lesser. It has been found by other researchers that, if sampling to altitudes of 50 km up is required, strong cryogenic pumping is necessary. This has been achieved on some balloon flights using liquid Helium for grab sampling purpose. The continuous sampling will, under vacuum, work up to the pumping limit of 0.5 m/m Hg, but the actual volume of gas taken in at high altitude will be minimum. In both cases, the pumping action of the 5A molecular sieve will help the pumping action by its absorption capability to gases.

Upon sealing and return, sample tubes in the module will be taken to the lab for analysis of the ampules. Analyses will be performed by bake out and pressure equalization into a gas chromatograph-mass spectrometer combination. The bake out is to be performed using a heating mantle around the grab sampler or continuous sampling tube, respectively.



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FIGURE 1

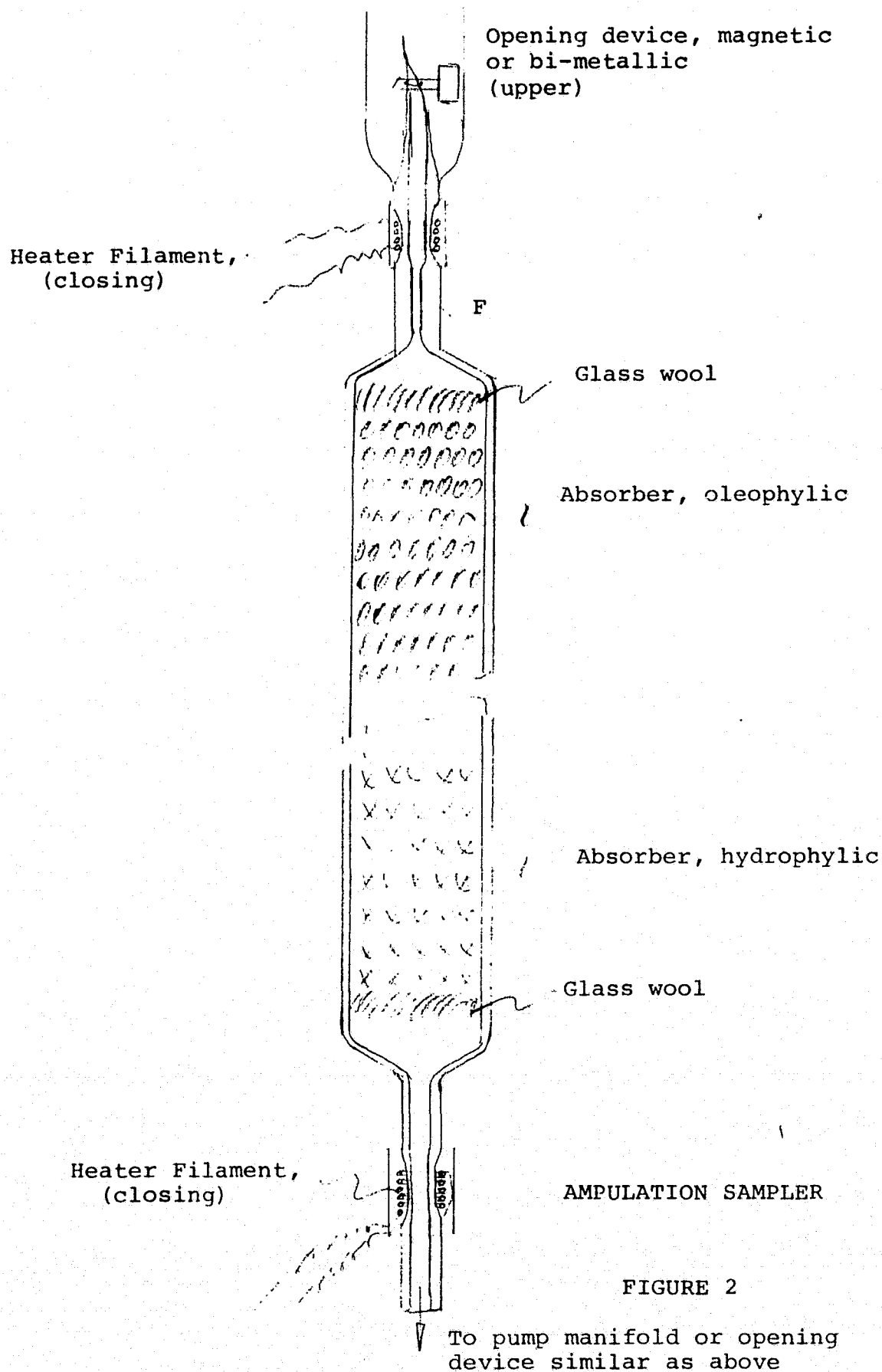


FIGURE 2

CONCLUSIONS

The use of valves in the design of gas sampling devices exposed to orbital flights has to be eliminated; leakage introduces an uncontrollable factor into the gas analysis. It is suggested that a design of an ampulation system which opens and/or closes at pre-set times and altitudes is needed for a sampling device.

Methods of analysis are: for lower altitude, gas sampling tubes for post-flight analysis with a gas chromatograph-mass spectrometer combination; for higher altitude, open-design mass spectrometer is proposed as flight hardware.

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General

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qualitative separation of mixtures of reactive gases (NO , NO_2 , SO_2 , HCl , H_2S , Cl , NH_3) and other gases (CO_2 , N_2O) in air was evaluated. Specifications for each column is given, and retention time for each gas as well as the order of elution is stated.

2. Nov. Obl. Prom. - Sanit. Khim, 1969, 60-71, a commercially produced automatic gas analyzer (FL5101) is based on light absorption in the reflection by a paper tape on which a color reaction of the detected gas with a suitable reagent proceeds. Detectable are NO , NO_2 , H_2S , NH_3 , Cl , HCl , H_2SO_4 (mist), F_2 , HF , O_3 , CS_2 , PH_3 , SbH_3 , AsH_3 , As , Hg , Pb^{4+} , CO , COCl_2 , CCl_4 , Freon, Hydrocarbons and moisture.

REFERENCES

1. Vertical Profiles of CH₄, H₂, CO, N₂O, and CO₂ in the Stratosphere, D. H. Ehhalt, L. E. Heidt, R. H. Lueb, and N. Roper, National Center for Atmospheric Research, Boulder, Colorado - U. S. Department of Transportation, Third Conference on CIAP, February, 1974, pg. 153.
2. Balloon-Borne Low Temperature Air Sampler, R. A. Lueb, D. H. Ehhalt, and L. E. Heidt, National Center for Atmospheric Research, Boulder Colorado - Rev. Sci. Instrum., Vol. 46, No. 6, June 1975, pg. 702.
3. Concentration and Analysis of Organic Volatiles in Skylab 4, W. Bertsch and A. Zlatkis, H. M. Liebich and H. J. Schneider, Chemistry Department, University of Houston, Houston, Texas 77004. Journal of Chromatography, 99, 1974, pg. 673-687.
4. Effect of Water, Vapour in the Quantitation of Trace Components Concentrated by Frontal Gas-Chromatography on TENAX-GC, J. Janak, J. Ruzickova and J. Novak, Journal of Chromatography, 99 (1974), pp. 689-696/

APPENDICES

APPENDIX A

FIGURES

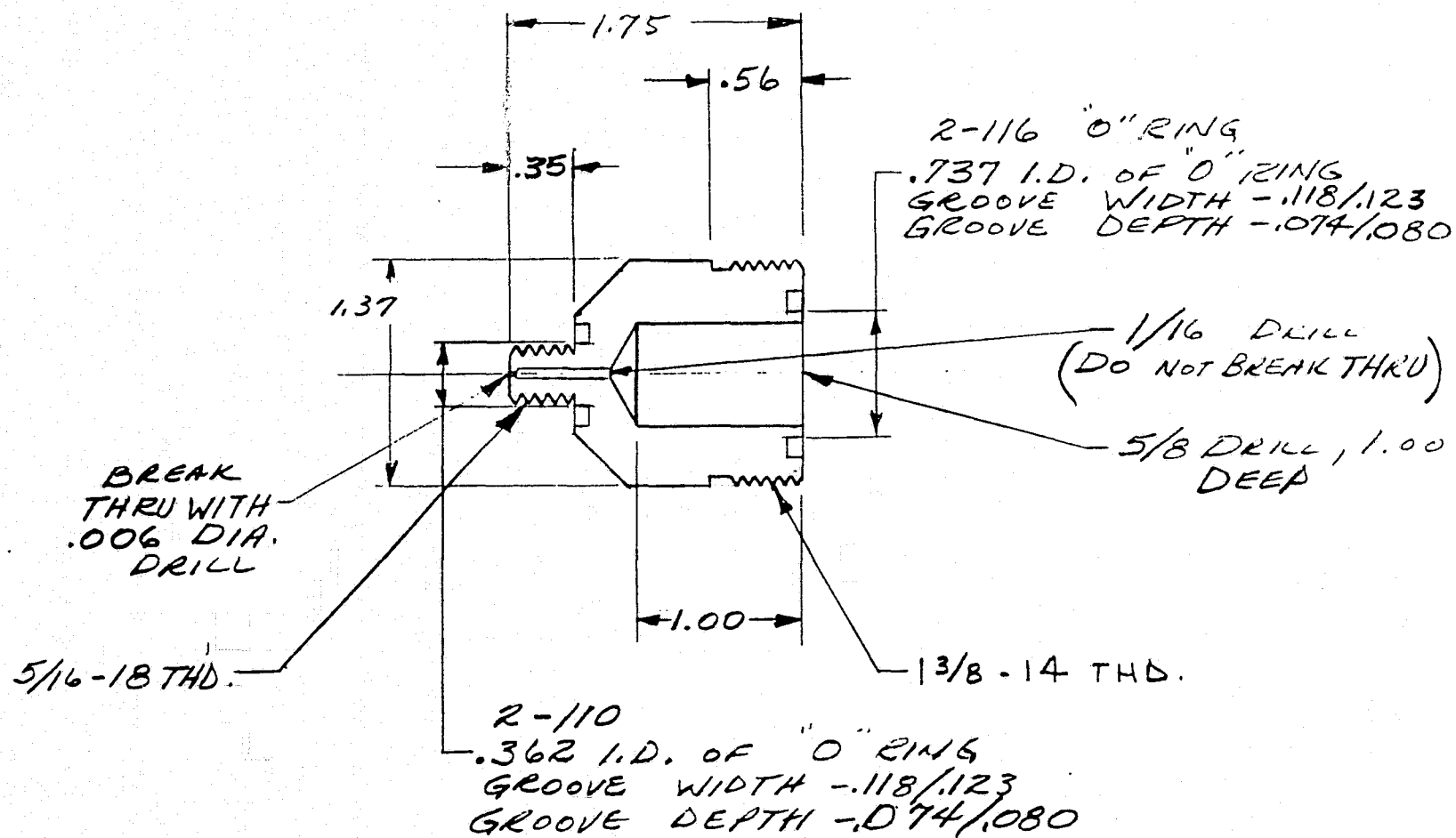


Figure 3. Ethylene Bottle

ETHYLENE BOTTLE
 MAT'L - KEL "F"
 SCALE - 1/1
 2 REQD.

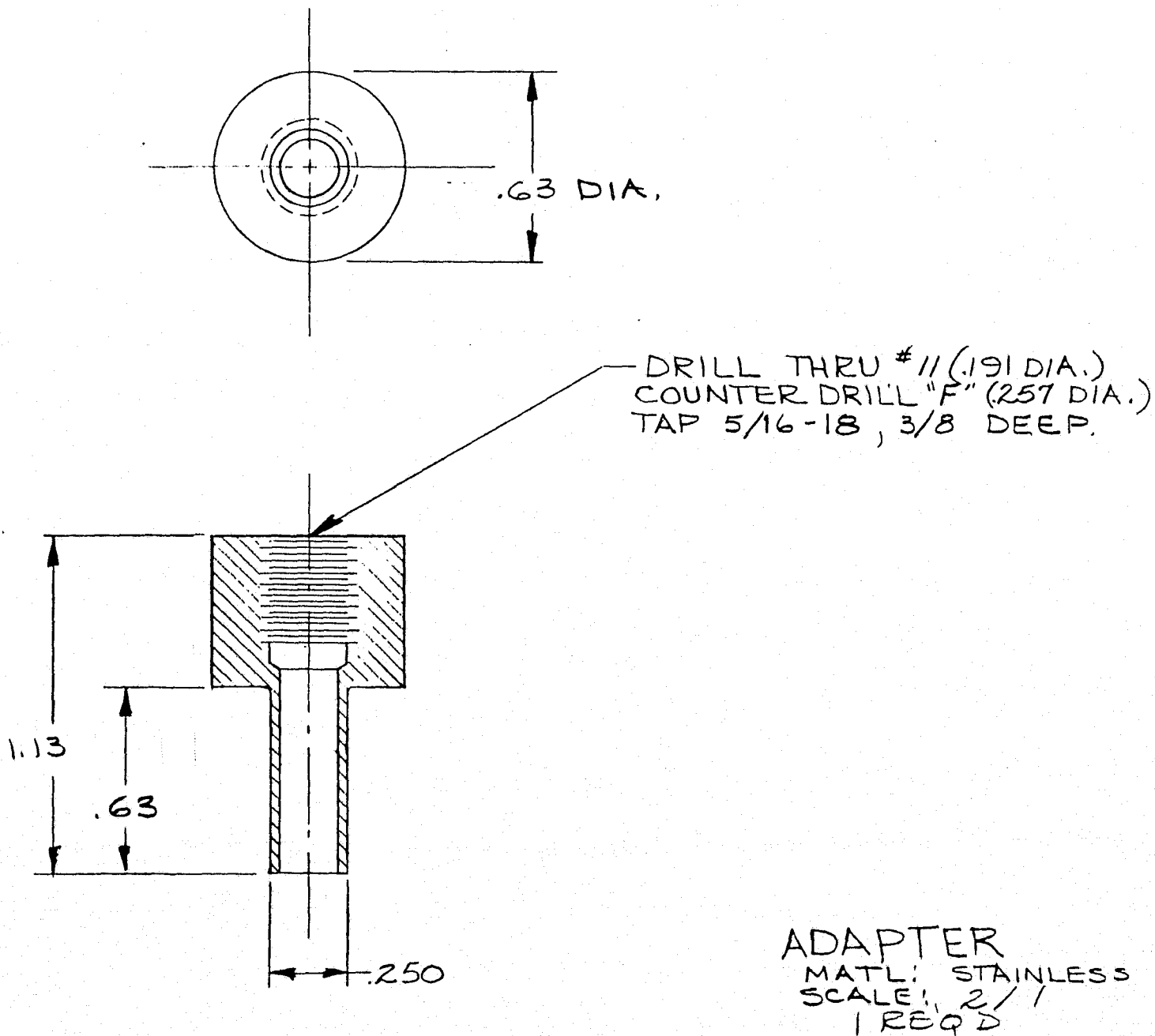
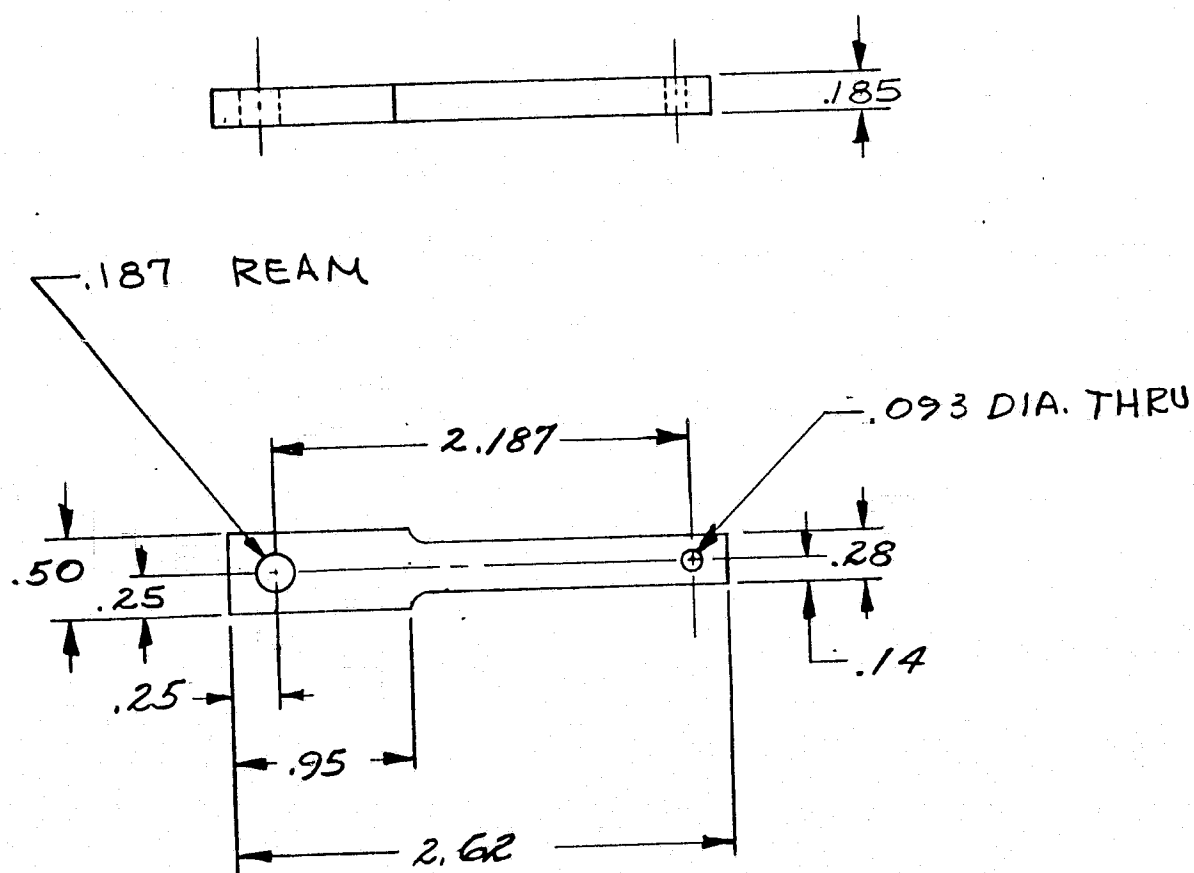
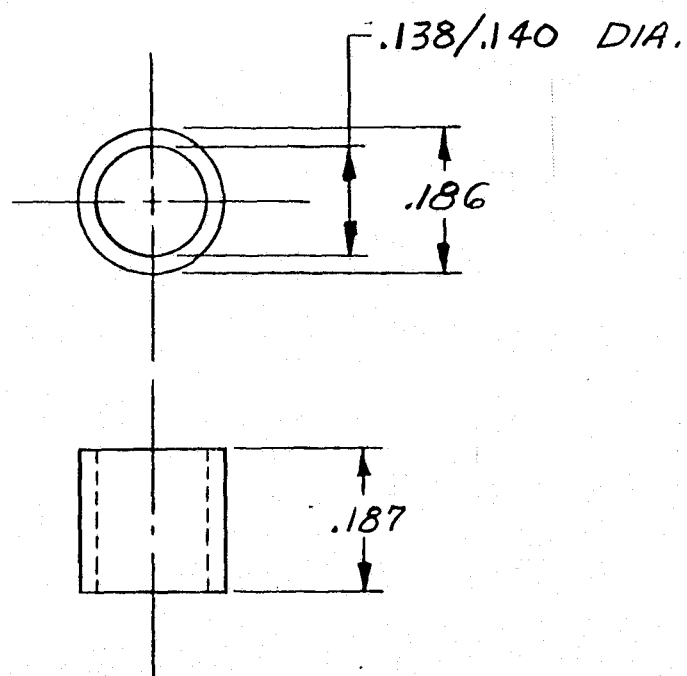


Figure 4. Adapter



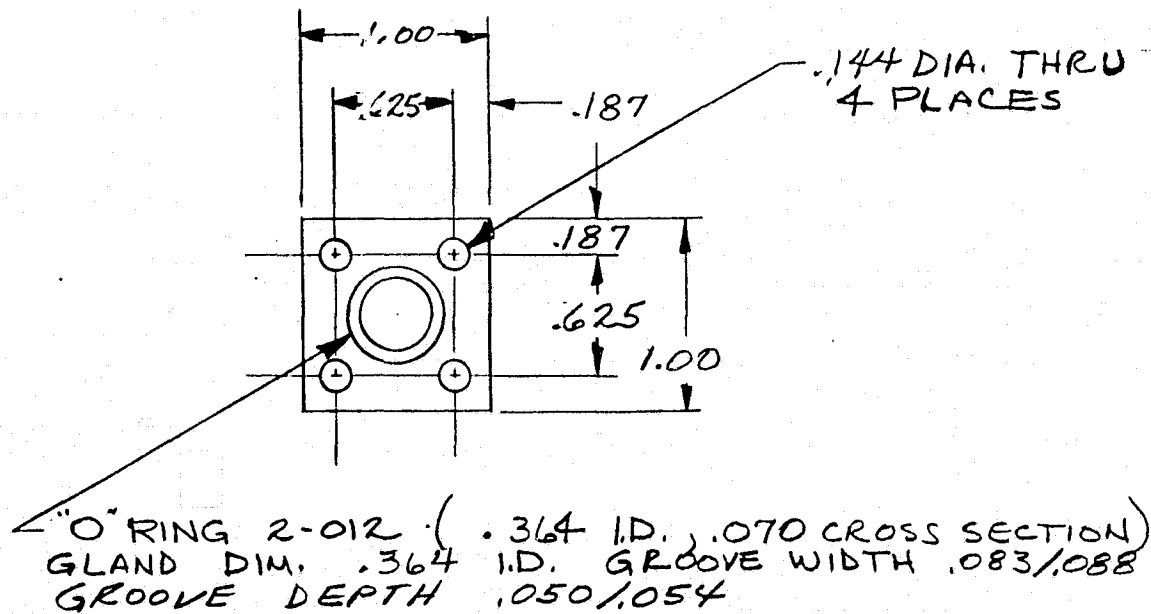
LINK, CAM
 MATL: KEL "F"
 SCALE: 1/1
 1 REQ'D

Figure 6. Link, Cam



BUSHING
MAT'L : STAINLESS STEEL
SCALE: 4/1
1 REQ'D

Figure 7. Bushing



CAP, END
 SCALE: 1/1
 MATL: KEL "F", 3/16 THK
 2 REQ'D

Figure 8. Cap, End

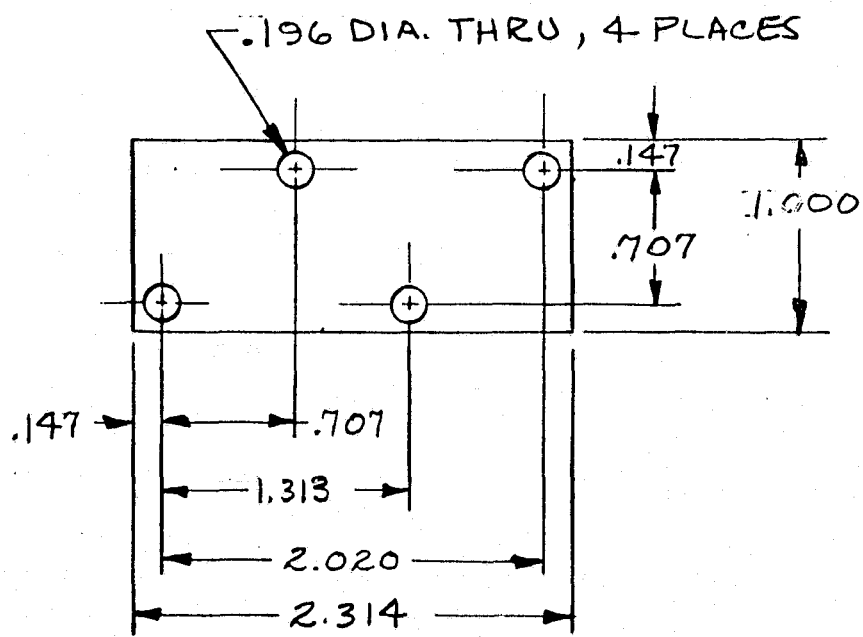
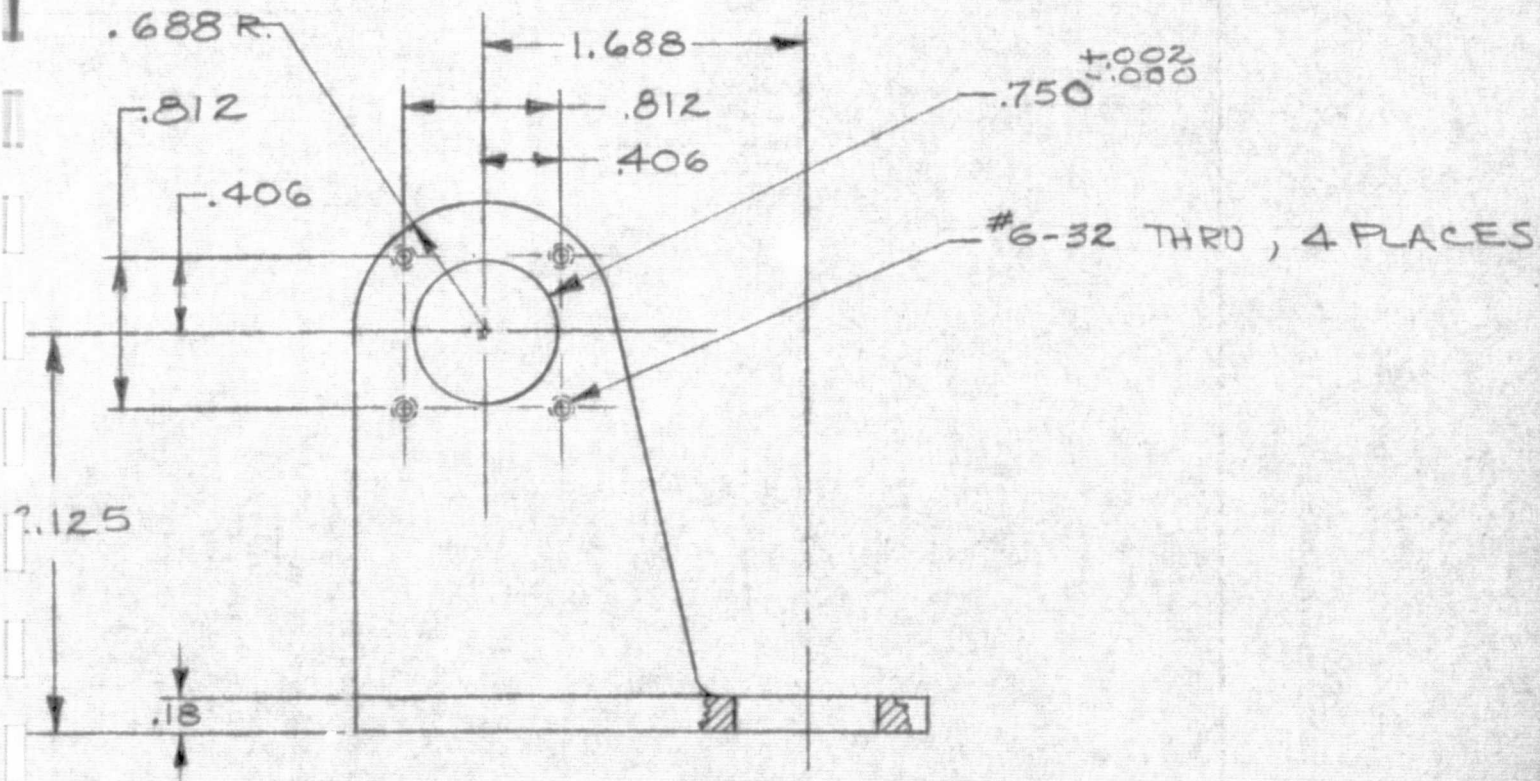
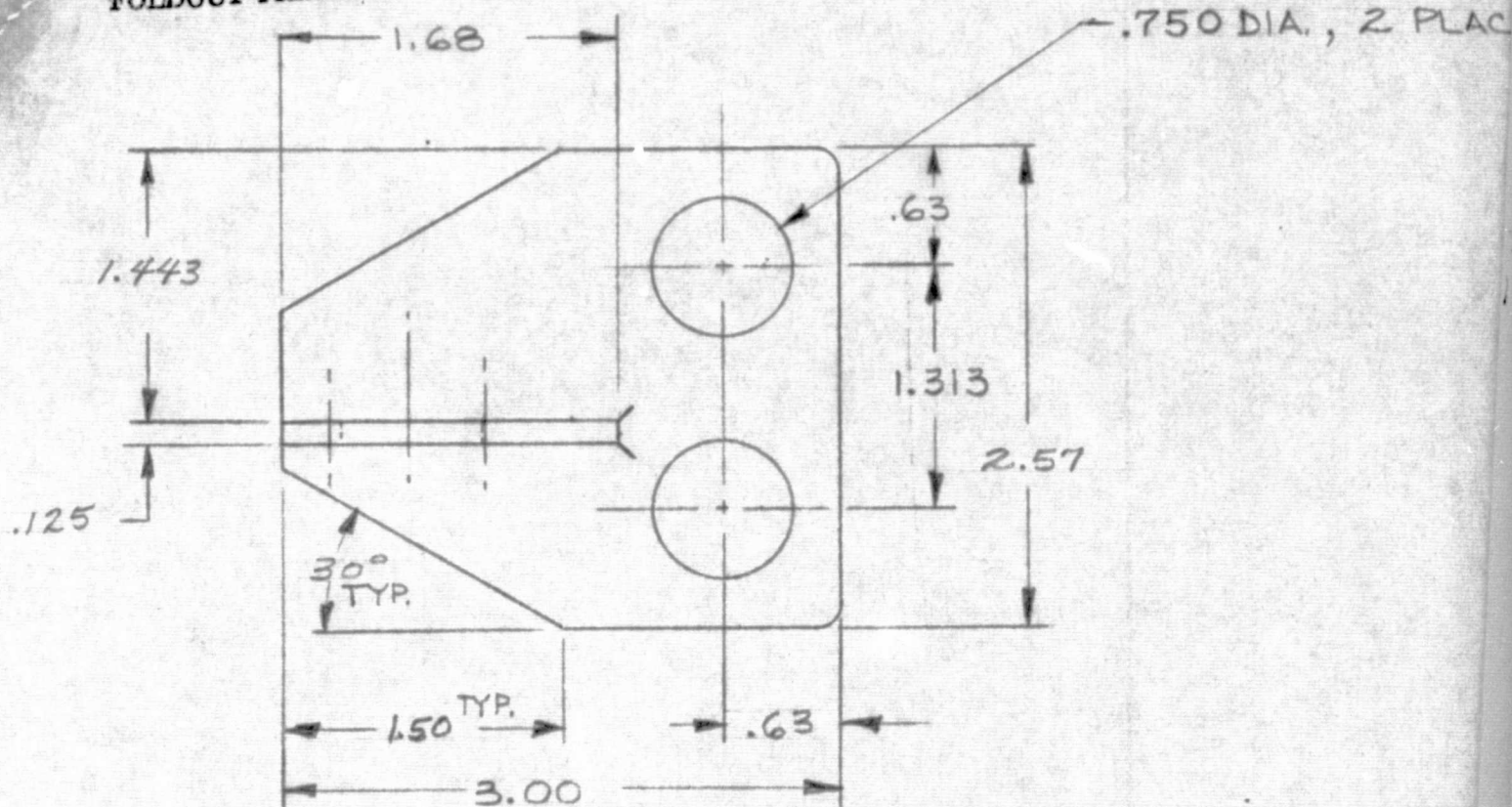


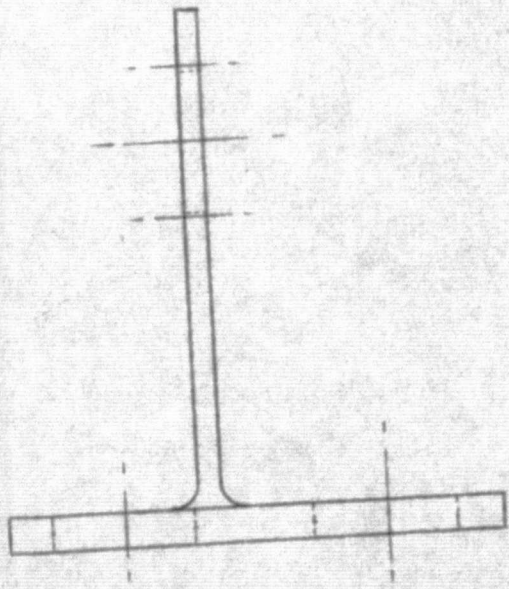
PLATE , MOUNTING
 SCALE: 1/1
 MATL : ALUM. ALLOY, 1/8 THK
 1 REQ'D

Figure 9. Plate, Mounting

FOLDOUT FRAME



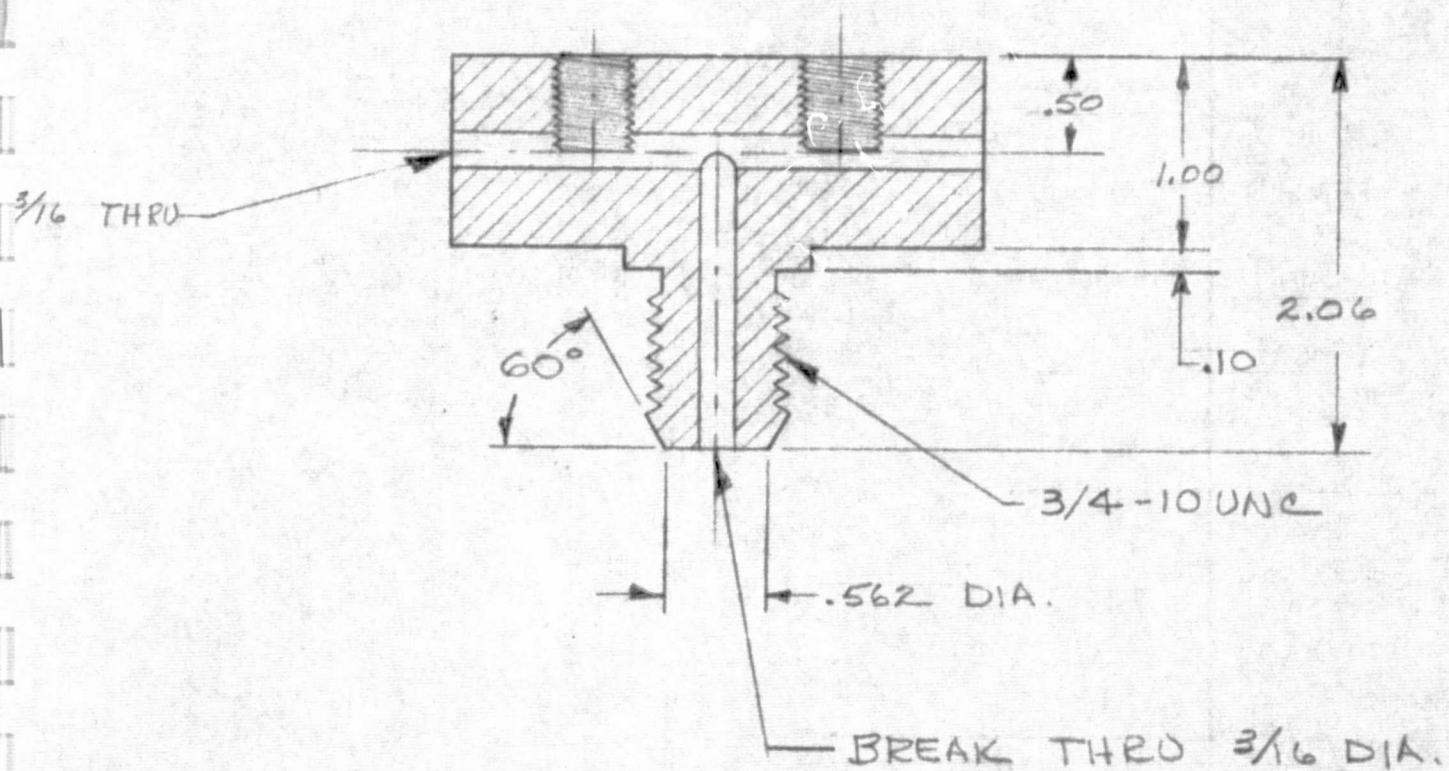
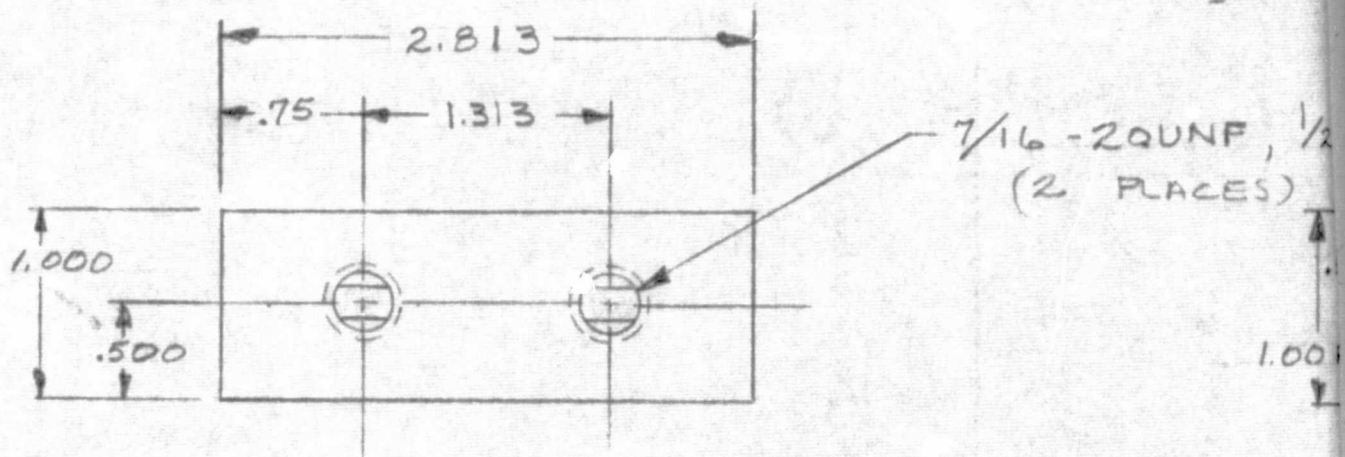
ES

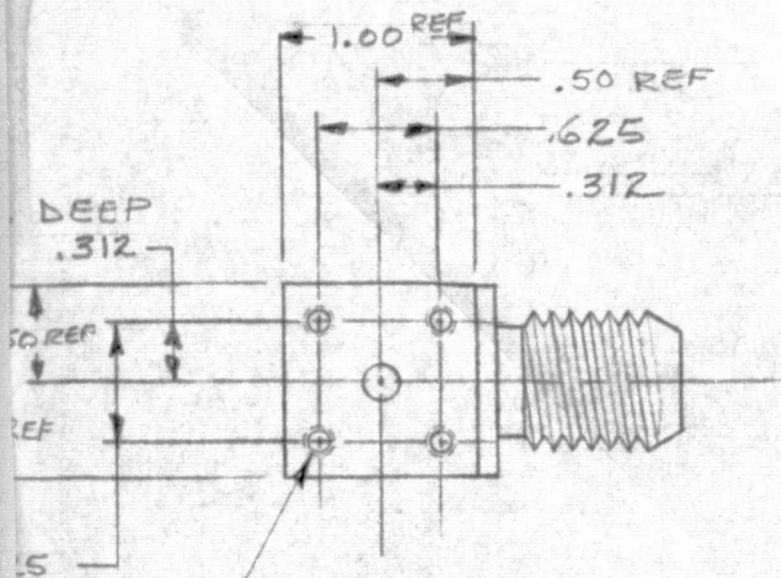


BRACKET, MOTOR MOUNTING
SCALE: 1/1
MATERIAL: ALUM. ALLOY
1 REQ'D

Figure 10. Bracket, Motor Mounting

FOLDOUT FRAME





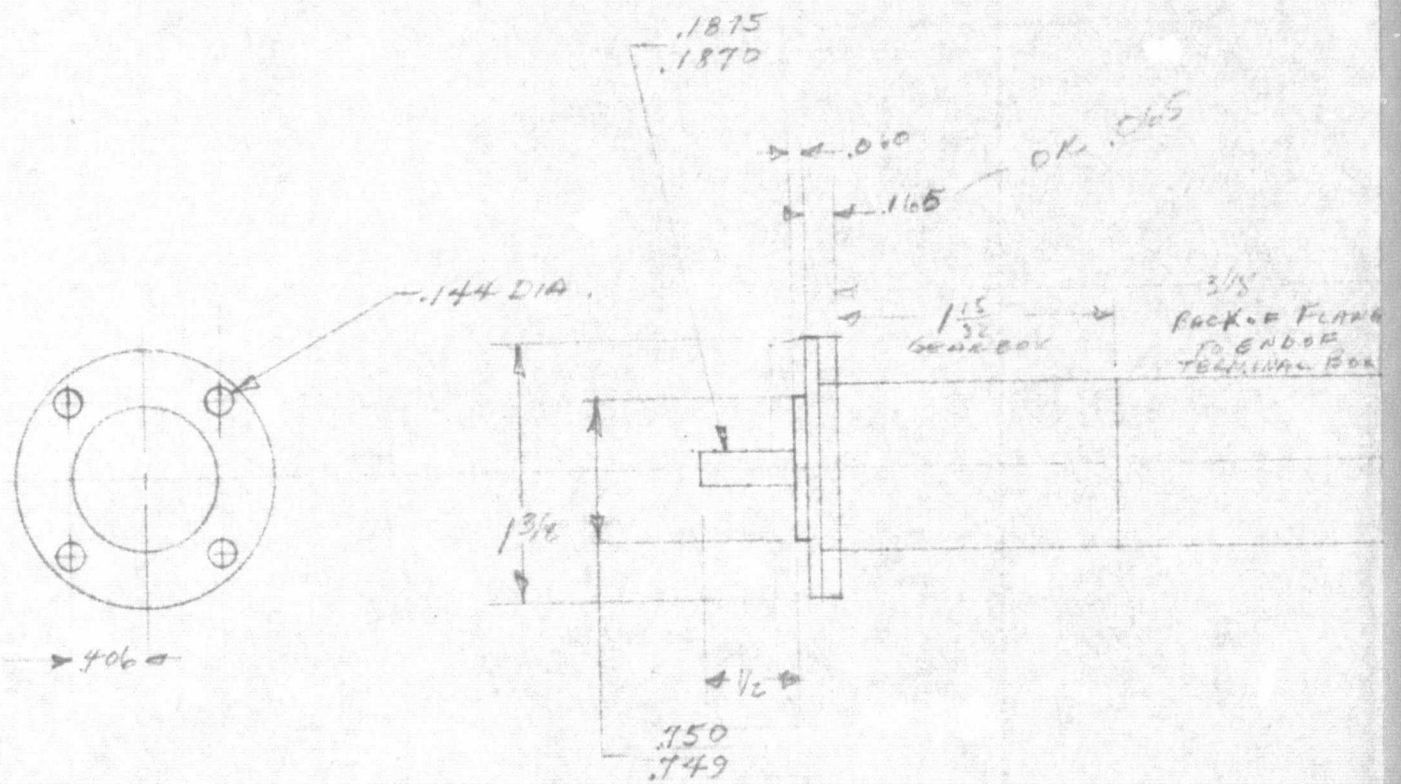
REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

#6 - 32 UNC, 3/8 DEEP 4 PLACES
(TYPICAL)

BLOCK, VALVE
SCALE: 1/1
MAT'L: KEL'F
1 REQ'D

Figure 11. Block, Valve

FOLDOUT FRAME



REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

8.000.000

7/8

8.02 WEIGHT

#17925

SS TYPE 2TVCC

PART No. 43A149-2

CF SHIELD

15 RPM. 333 RPM

BARON PROTECT LUB

IN BEARINGS

BRUSHES MAKE

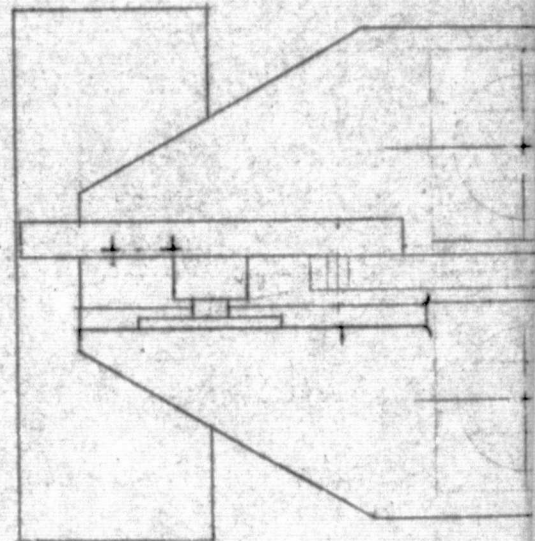
BY FINE CARBON

COMPANY

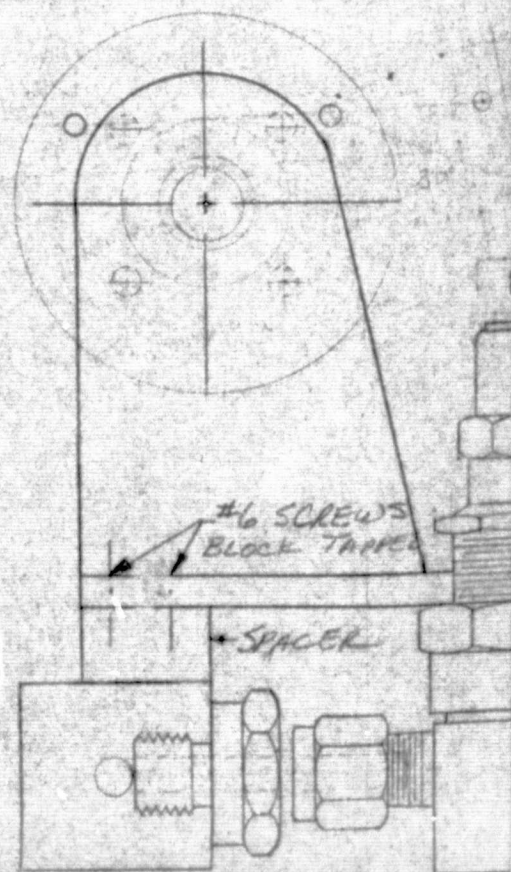
GOOD TO 10,000 HRS

Figure 12. Motor

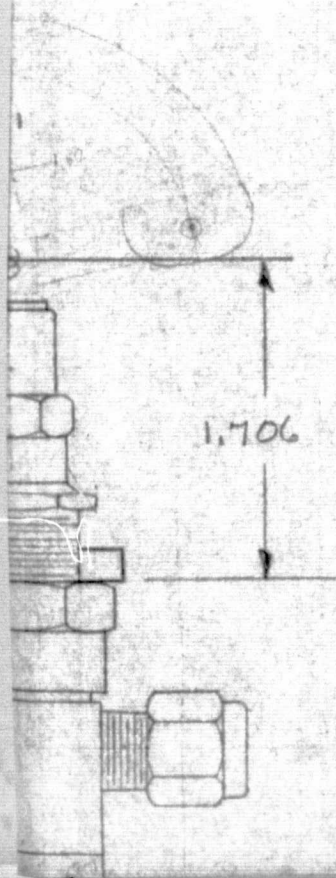
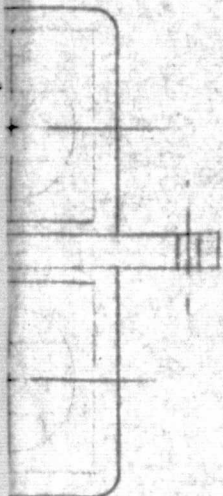
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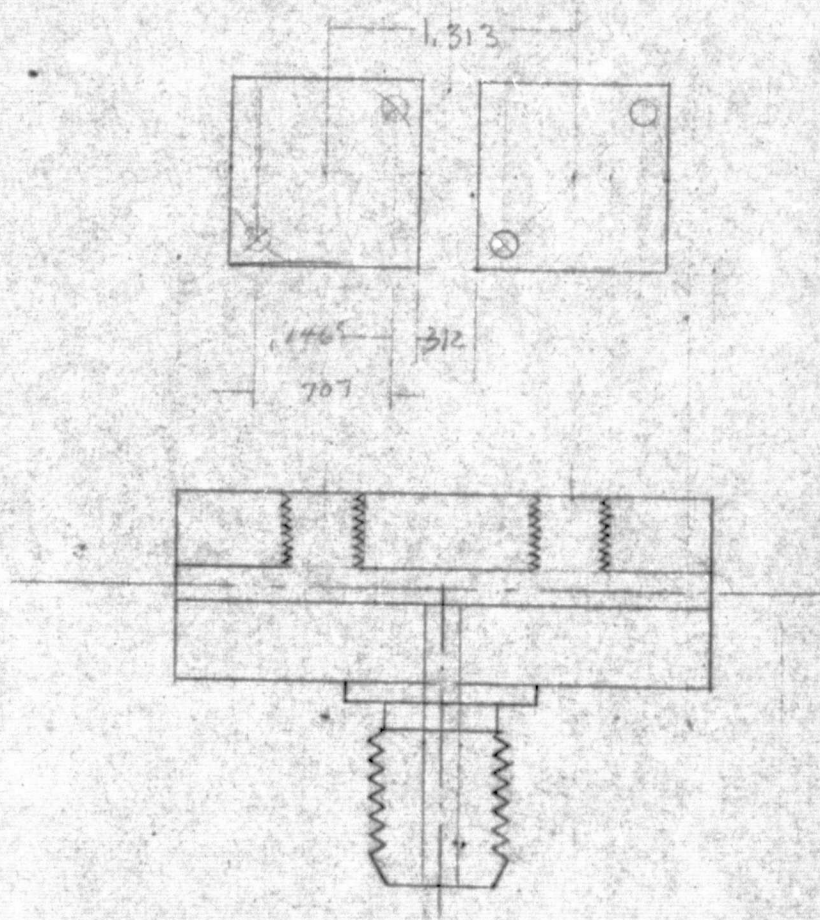
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FOLDOUT FRAME 2



FOLDOUT FRAME 3



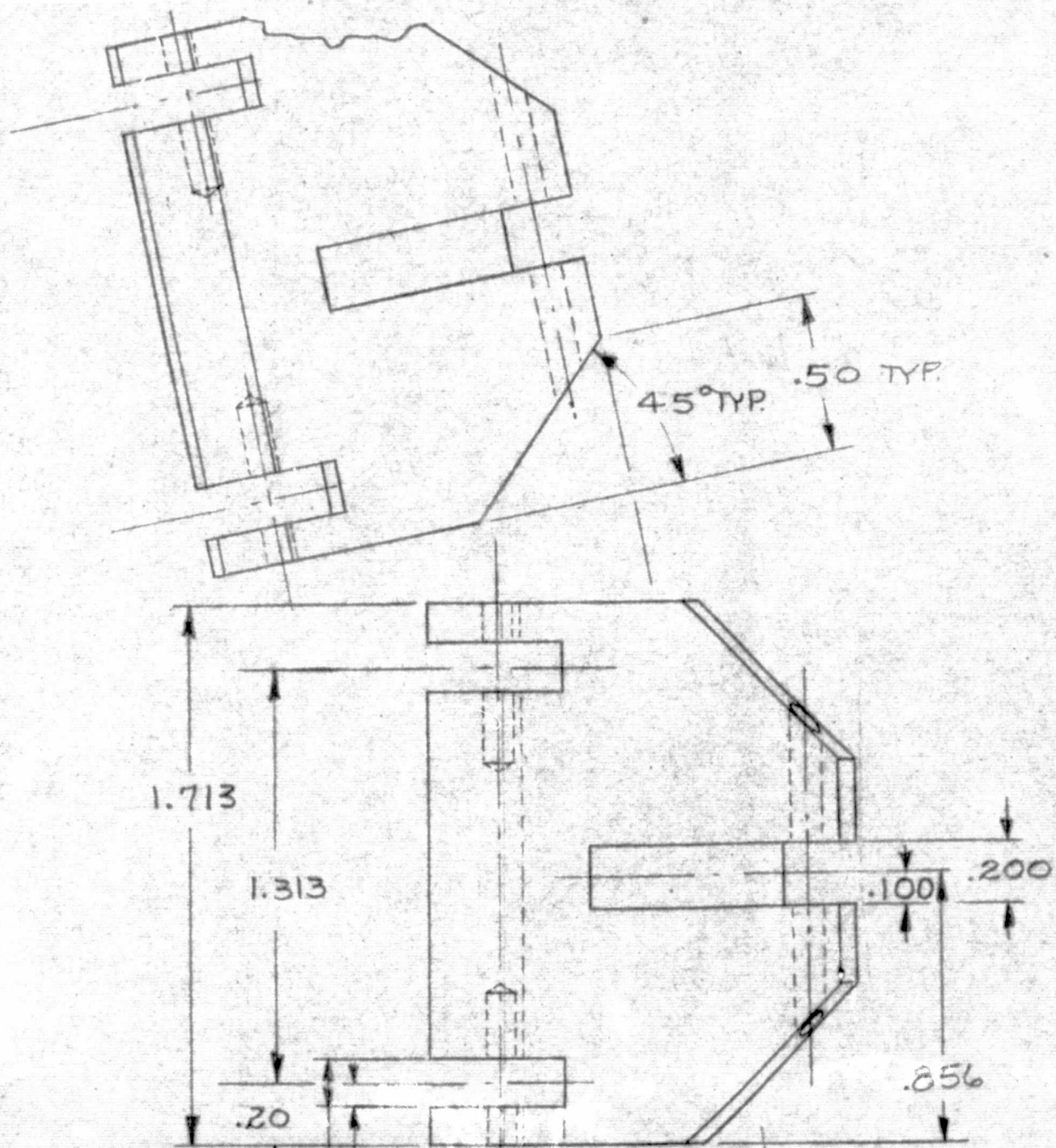
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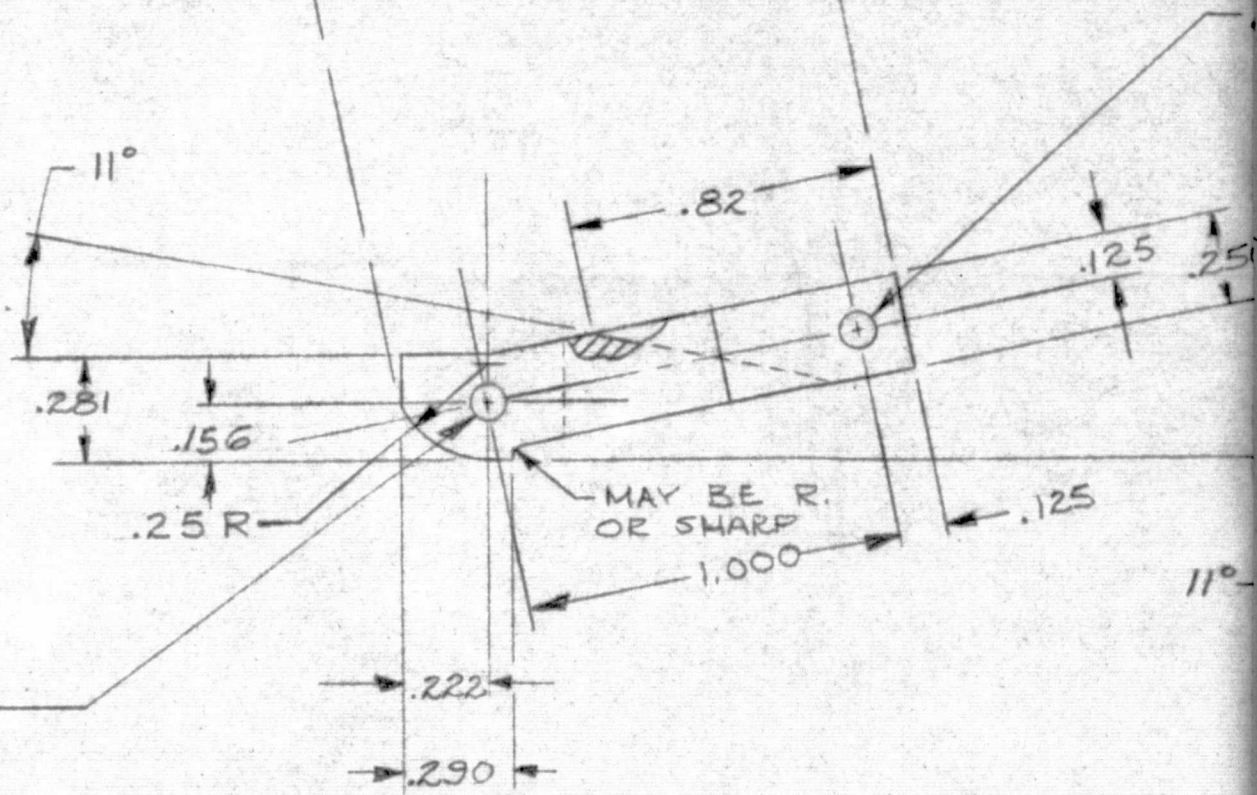
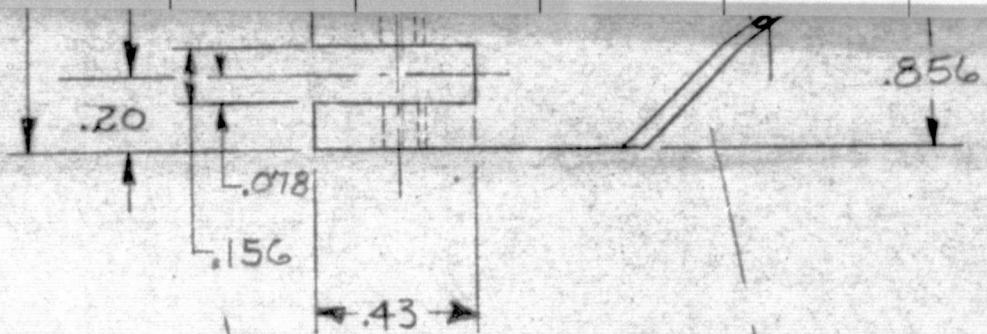
REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR

Figure 13. Assembly Detail

OUT FRAME



FOLDOUT FRAME
 FRAME 2



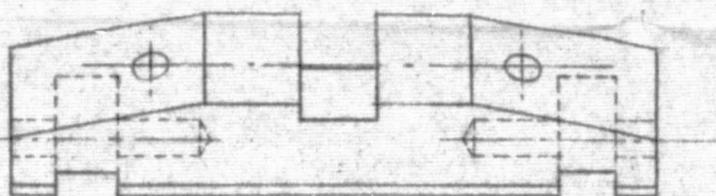
093 DIA. , .75 DEEP
 TYPICAL 2 PLACES

MAY BE R.
 OR SHARP

.093 DIA. THRU

250

11°



CAM, VALVE
MAT'L : KEL-F
SCALE : 2/1
1 REQ'D

Figure 14. Cam Valve

APPENDIX B

PORAPAK

Porapak

GAS CHROMATOGRAPHY COLUMN PACKING MATERIALS

PORAPAK, manufactured by Waters, is used by thousands of gas chromatographers as the preferred packing material for performing a variety of difficult separations. These porous polymer beads provide sharp symmetrical peaks and low retention volumes for polar materials such as water, alcohols, acids, and glycols. PORAPAK has the partition properties of a highly extended liquid without the problems of support polarity, liquid phase volatility, or freezing point which normally restrict gas liquid chromatography.

Eight types of PORAPAK are provided in a broad range of mesh sizes, each with significantly different functionality and retention properties. In order of increasing polarity (water eluting later), the eight PORAPAK'S are P, P-S, Q, Q-S, R, S, N, and T. The P-S and Q-S packings are silane-treated PORAPAK P and Q, respectively and are similar in relative retention characteristics to the parent PORAPAK. Silanization virtually eliminates peak tailing and ghosting with very polar materials.

- PORAPAK P — Least polar / separates a wide variety of carbonyl compounds / stable to 250° C.
- PORAPAK P-S — Surface silanized version of "P" eliminates tailing and ghosting / particularly effective for separating aldehydes and glycols / stable to 250° C.
- PORAPAK Q — Most widely used / hydrocarbon structure / particularly effective for separating aliphatic hydrocarbons / stable to 250° C.
- PORAPAK Q-S — Surface silanized version of "Q" / separates organic acids and other polar compounds without tailing / stable to 250° C.
- PORAPAK R — Moderate polarity / long retention and good resolution for ethers/stable to 250° C.
- PORAPAK S — Excellent for separating normal and branched alcohols / stable to 250° C.
- PORAPAK N — Separates ammonia in aqueous streams / and acetylene from other C₂ hydrocarbons / exhibits high water retention / stable to 190° C.
- PORAPAK T — Highest polarity and greatest water retention of the PORAPAK series for determining formaldehyde in aqueous samples / stable to 190° C.

PORAPAK is used for all gases and most compounds in the moderate boiling range (up to 250° C) with some applications for compounds boiling as high as 350° C. Using temperature programming, wide boiling range mixtures can be analyzed with a single column. Relative retention data of the eight types of PORAPAKS at 30° C and 175° C are listed in the following tables.

RELATIVE RETENTION OF PORAPAK COLUMN PACKINGS

1 meter x 2.2 mm ID column

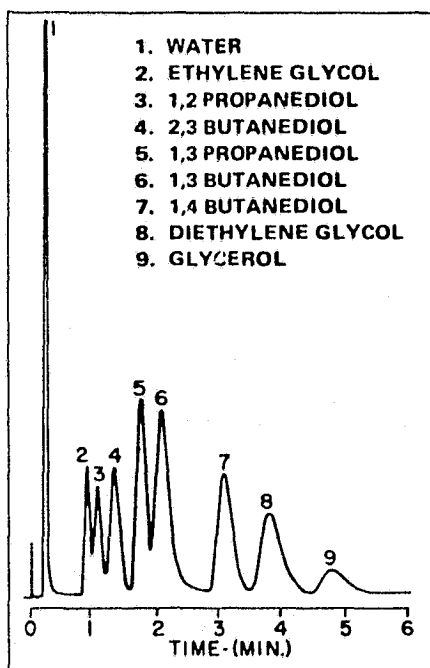
Temp = 175°C

Flow Rate = 25 ml/min

Detector = FID (except TC for water)

SAMPLE	P	P-S	Q	Q-S	R	S	N	T
Water	0.467	0.408	0.056	0.082	0.131	0.109	0.135	0.188
Methanol	0.542	0.475	0.127	0.134	0.180	0.168	1.193	0.244
Formaldehyde	0.517	0.475	0.134	0.127	0.190	0.172	0.195	0.172
Acetaldehyde	0.542	0.475	0.169	0.170	0.190	0.187	0.222	0.259
Ethanol	0.666	0.592	0.218	0.230	0.307	0.291	0.367	0.462
Formic acid	0.717	0.717	0.225	0.189	0.368	0.386	0.819	0.187
Acetonitrile	0.934	0.792	0.287	0.286	0.358	0.348	0.497	0.670
Propylene oxide	0.784	0.666	0.314	0.327	0.336	0.329	0.406	0.444
Propionaldehyde	0.808	0.750	0.338	0.343	0.376	0.383	0.476	0.543
Acetone	0.850	0.758	0.343	0.349	0.390	0.391	0.544	0.666
Isopropanol	—	—	0.351	—	—	—	—	—
Methylene chloride	0.950	0.960	0.373	0.403	0.407	0.438	0.510	0.545
Acrylonitrile	1.00	0.892	0.388	0.404	0.474	0.475	0.660	0.853
Acetic acid	1.03	0.926	0.419	0.379	1.31	1.91	1.34	1.90
Methyl acetate	0.883	0.800	0.419	0.434	0.445	0.438	0.598	0.735
Propanol	0.984	0.883	0.479	0.478	0.660	0.641	0.862	1.06
Pentane	0.684	0.666	0.501	0.536	0.481	0.469	0.490	0.467
Isobutyraldehyde	1.05	0.934	0.598	0.623	0.670	0.676	0.905	1.04
Butyraldehyde	1.22	1.10	0.711	0.710	0.776	0.802	1.09	1.28
2-Butanone	1.26	1.18	0.734	0.730	0.820	0.846	1.20	1.41
Chloroform	1.35	1.28	0.753	0.718	0.854	0.791	0.966	1.24
Ethyl acetate	1.22	1.13	0.812	0.852	0.864	0.862	1.20	1.44
Isobutanol	1.36	1.26	0.902	0.900	1.24	1.21	1.76	2.07
Propionic acid	1.67	1.53	0.909	0.843	—	—	—	4.27
Hexane	1.00 (0.945min)	1.00 (0.944min)	1.00 (4.93min)	1.00 (5.50min)	1.00 (4.67min)	1.00 (4.97min)	1.00 (6.94min)	1.00 (4.84min)
Butanol	1.58	1.48	1.07	1.07	1.47	1.46	2.08	2.50
Benzene	1.86	1.69	1.16	1.16	1.24	1.25	1.42	1.67
Carbon tetrachloride	1.53	1.53	1.16	1.14	1.07	1.07	1.17	1.34
Isopropyl acetate	1.46	1.47	1.33	1.43	3.48	1.44	2.04	2.38
Propyl acetate	1.83	1.85	1.72	1.83	4.20	1.83	2.64	3.19
Isopentanol	2.27	2.29	2.10	2.09	2.91	2.85	4.25	5.10
Heptane	1.58	1.64	2.28	2.28	2.18	2.05	2.18	2.20
Pentanol	2.63	2.61	2.46	2.46	3.38	3.35	4.93	5.86
Toluene	3.18	2.92	2.71	2.69	2.43	2.85	3.24	3.65

REPRESENTATIVE PORAPAK CHROMATOGRAMS

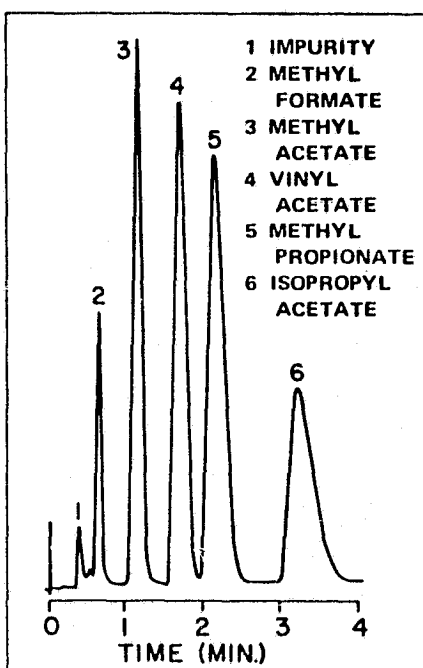
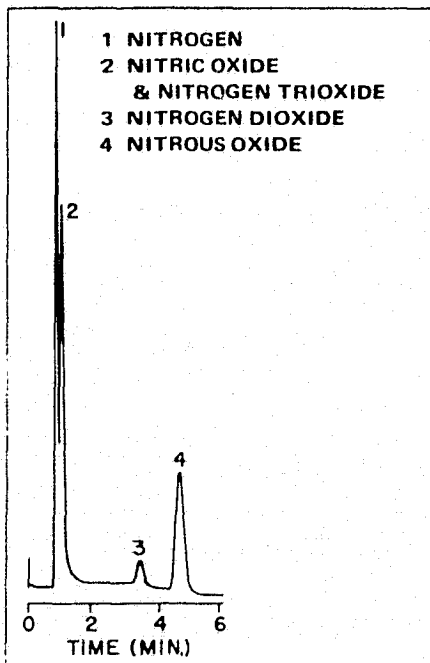


GLYCOLS

COLUMN: 1 m x 2.3 mm; SUPPORT: PORAPAK P, 80/100 mesh; CARRIER: Helium, 30 ml/min; DETECTOR: TC; TEMPERATURES: Injector 300°C, Column 200°C, Detector 300°C

COLUMN: 8 ft x 2.3 mm; SUPPORT: PORAPAK Q, 80/100 mesh; CARRIER: Helium, 20 ml/min; DETECTOR: TC; TEMPERATURES: Injector 150°C, Column 23°C, Detector 200°C

OXIDES OF NITROGEN

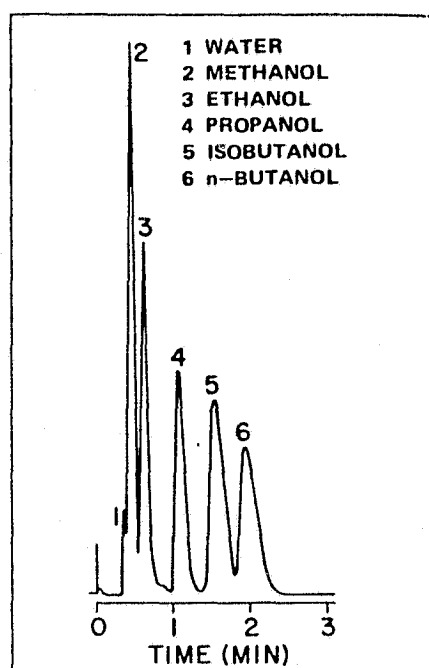
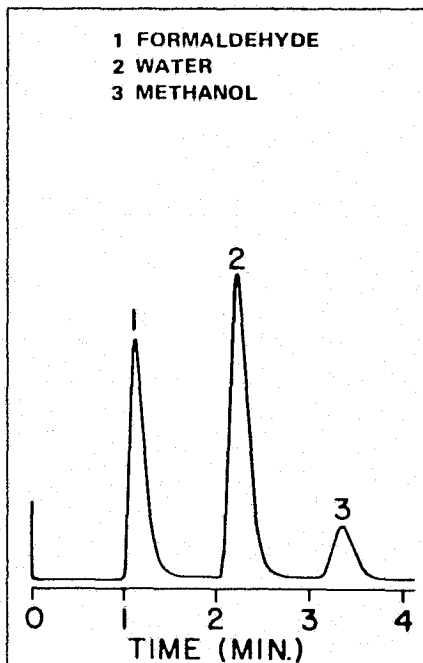


ESTERS

COLUMN: 1 m x 2.3 mm; SUPPORT: PORAPAK R, 80/100 mesh; CARRIER: Helium, 30 ml/min; DETECTOR: TC; TEMPERATURES: Injector 300°C, Column 190°C, Detector 300°C

COLUMN: 1 m x 2.3 mm; SUPPORT: PORAPAK T, 80/100 mesh; CARRIER: Helium, 25 ml/min; DETECTOR: TC; TEMPERATURES: Injector 300°C, Column 140°C, Detector 300°C

FORMALDEHYDE - WATER

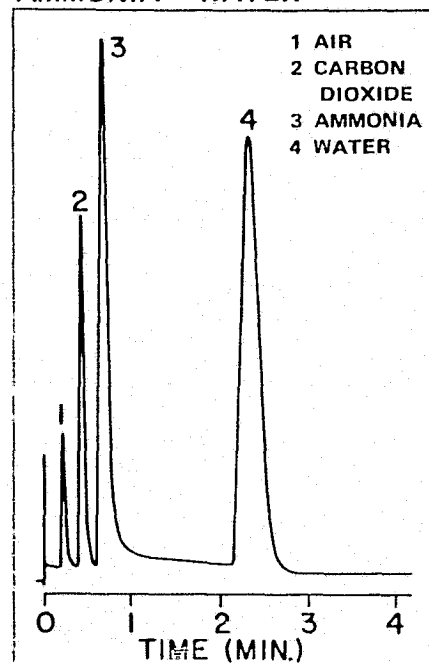


ALCOHOLS

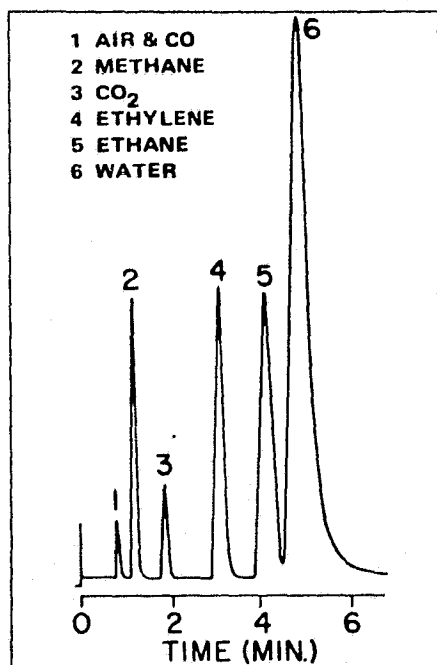
COLUMN: 1 m x 2.3 mm; SUPPORT: PORAPAK P, 80/100 mesh; CARRIER: Helium, 25 ml/min; DETECTOR: TC; TEMPERATURES: Injector 300°C, Column 160°C, Detector 300°C

COLUMN: 1 m x 2.3 mm; SUPPORT: POROPAK N, 80/100 mesh; CARRIER: Helium, 25 ml/min; DETECTOR: TC; TEMPERATURES: Injector 300°C, Column 120°C, Detector 300°C

CARBON DIOXIDE - AMMONIA - WATER



PORAPAK FEATURES

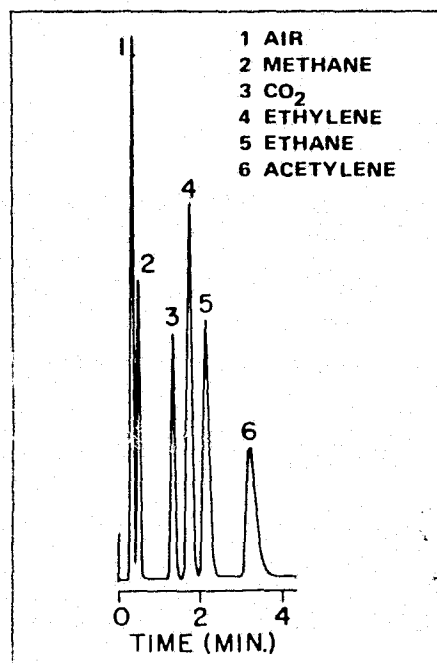


HYDROCARBONS IN WATER

COLUMN: 8 ft x 2.3 mm; SUPPORT: PORAPAK Q, 80/100 mesh; CARRIER: Helium, 20 ml/min; DETECTOR: TC; TEMPERATURES: Injector 150°C, Column 50°C, Detector 200°C

COLUMN: 1 m x 2.3 mm; SUPPORT: PORAPAK N, 80/100 mesh; CARRIER: Helium, 25 ml/min; DETECTOR: TC; TEMPERATURES: Injector 150°C, Column 50°C, Detector 200°C

C₁ - C₂ HYDROCARBONS



No Bleed from the Packing Materials

Separation results from the porous polymer nature of the beads. Since the polymer beads are usually not coated, baseline stability of the chromatograph is extremely good even with high sensitive detectors and high column temperatures.

No Adsorption of Polar Compounds

The porous polymer beads have very large surface areas but still do not react with polar materials. Polar compounds such as water, alcohols, acids, and glycols are eluted rapidly through PORAPAK as sharp symmetrical peaks.

Stable at High Temperatures

The rigid cross-linked polymers can be used at high temperatures before polymer degradation occurs. It is therefore possible to temperature program columns from a very low temperature to high temperatures for wide boiling range samples.

No Change in Retention Time

PORAPAK is inert to almost all polar compounds, stable at high temperatures, and not subject to bleeding -- there is no tendency to change retention time or peak shape.

Separation of Water from Organic Materials With PORAPAK Q

Water is not absorbed by the lipophylic polymer beads. The water peak elutes between ethane and propane on PORAPAK Q and does not tail (the bead acts like water had a boiling point of -20°C). Hydrocarbon separations can be made where there is a water contaminant.

PORAPAK is ideal for separating traces of water from organic liquids. On PORAPAK Q, water elutes well before any organic liquid peak. (See Table of Relative Retention.) As a result, heavy overloading of organic liquids does not mask the earlier water peak. Trace water can be detected using a moderate sensitivity thermal conductivity detector because PORAPAK elutes water early and rapidly recovers from the high overload of organic liquid.

Analysis of Gases Using PORAPAK Q

Another advantageous feature of PORAPAK is that it elutes water with the light hydrocarbon gases. Since there are only a few hydrocarbon gases, water is easily separated as a separate sharp peak. This permits the detection of water in light gases simultaneously with the detection of the light gases and heavier organics. It is not necessary to use dual column operation in order to accurately detect water in the presence of light or heavy organic gases or liquids.

Large Surface Area

PORAPAK has a surface area from 50 to 600 square meters per gram. This high surface area, plus the absence of OH adsorption, increases the applicability of PORAPAK as a support for liquid coatings or as a column packing material for a wide variety of separations.

Coating of the Beads

For increased versatility, PORAPAK can also be coated with any of the normal liquid coatings. The high surface area of the beads makes possible unique liquid coated separations.

Easy Column Packing With High Efficiency

PORAPAK polymer beads are rigid, can be handled easily, and packed into columns using normal packing techniques without crushing or fracturing. With standard techniques, column efficiencies of 400–800 plates per foot are obtained.

Rapid Overload Recovery

The separation made by the polymer beads is not based on conventional hydroxyl adsorption. PORAPAK's lipophylic adsorption permits large sample loads to be applied without excessive tailing. PORAPAK is extremely useful for both preparative and trace analysis chromatography.

PORAPAK

Catalog Number for each Type and Mesh Range

MESH	N	P	P-S	Q	Q-S	R	S	T
50-80	27047	27053	27083	27059	27089	27065	27071	27077
80-100	27048	27054	27084	27060	27090	27066	27072	27078
100-120	27049	27055	27085	27061	27091	27067	27073	27079
120-150	27050	27056	27086	27062	27092	27068	27074	27080
150-200	27051	27057	27087	27063	27093	27069	27075	27081
200-325	27052	27058	27088	27064	27094	27070	27076	27082
Temperature limit (°C)	190	250	250	250	250	250	250	190
PRICE	\$19.00	\$19.00	\$25.00	\$17.00	\$22.00	\$19.00	\$19.00	\$19.00

A package of PORAPAK contains 75 ml and is enough to fill 10 columns 6 feet x 1/8-inch OD